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⑳ Solventless silicone controlled release compositions.

㉑ Controlled release additives are provided which are useful to raise the release of low-release solventless silicone release compositions. Solventless silicone release compositions are also provided. The aged release of controlled release compositions may also be enhanced by addition of a small amount of a vinyl polysiloxane gum.

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SOLVENTLESS SILICONE CONTROLLED
RELEASE COMPOSITIONSBACKGROUND OF THE INVENTION

This invention relates to polysiloxane release
5 coating compositions. More particularly, it relates to low
viscosity polysiloxane compositions containing increased
amounts of MQ silicone resins without the need of solvents
which are particularly well-adapted to controlled release
applications.

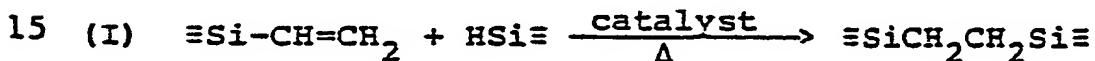
10 Silicone compositions have long been used as
release coatings, which are useful in many applications
whenever it is necessary to provide a surface or material
which is relatively nonadherent to other materials which
would normally adhere thereto. Silicone release composi-
15 tions are widely used as coatings which release pressure-
sensitive adhesives for labels, decorative laminates,
transfer tapes, etc. Silicone release coatings on paper,
polyethylene, Mylar®, and other such substrates are also
useful to provide non-stick surfaces for food handling and
20 industrial packaging applications.

25 Silicone compositions previously developed as
release coatings have included solutions in organic
solvents, water dispersed emulsions and solvent-free
("100 % solids") silicone fluids. The solventless
silicones are increasingly preferred for release
applications because of the energy inefficient evaporation
steps, solvent recovery and costly pollution abatement

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equipment associated with use of the solvent- and water-borne systems.

Solventless silicone release compositions, such as those taught by Eckberg, U.S. 4,256,870 (incorporated herein by reference), are typically two-part systems: One part is a mixture of a vinyl-containing linear diorganopolysiloxane, a precious metal catalyst and an inhibitor. The other part is a $\equiv\text{SiH}$ -containing crosslinker, such as a polymethylhydrogensiloxane fluid. These parts may be combined in a coating bath, applied to a substrate and cured to an adhesive coating by a thermally-accelerated addition cure reaction illustrated as follows:



Cured release coatings using 100% solids silicone compositions exhibit exceptionally low, or "premium", release, i.e., very little force is required to separate most adhesives from the silicone-treated surface. However, most commercial applications demand higher (or "tighter") release from common pressure-sensitive adhesives, and so additives, called "controlled-release additives" or "CRAs" are added to low-release compositions to raise their release.

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Branched silicone resins, such as vinyl-MQ silicone resins are typically employed as release-increasing agents in CRAs. Conventional CRA formulations, such as those described by Sandford, Jr., U.S. 4,123,664 and Keil, U.S. 3,527,659 (both incorporated herein by reference) contain up to 40-45% by weight vinyl-MQ resin (described in more detail infra) dissolved in a vinyl-functional diorganopolysiloxane, plus a catalyst and inhibitor.

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Although they currently enjoy widespread use, conventional solventless CRAs have major disadvantages resulting from their high cost and processing limitations. The vinyl-MQ resins cannot be incorporated into vinyl-functional polysiloxane fluids in amounts greater than about 40-45% by weight without exceeding a workable application viscosity: At such levels the resulting compositions have viscosities >5000 cps, 10 times the preferred viscosity for rotogravure application to papers or films. See, e.g., Moeller, U.S., 4,216,252 (incorporated herein by reference). Consequently, the MQ resin content of CRAs is held down, but then large amounts of these expensive materials are added to low release solutions to bring about a higher release. This necessity of using high levels of costly additives in conventional solventless controlled release compositions often makes their use prohibitively expensive, in spite of the energy costs and pollution abatement costs their use avoids.

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It has now been discovered that efficient, inexpensive solventless CRAs having low viscosities are formulated by dispersing MQ or vinyl-MQ silicone resins in high-boiling, unsaturated reactive diluents. The olefinic materials are less expensive than polysiloxane fluids and their low viscosities permit high levels of the MQ resins to be dispersed.

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SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide controlled release additives which 5 may contain above about 40% by weight MQ silicone resin while maintaining a low application viscosity.

It is a further object of the present invention to provide a solvent-free silicone release coating 10 composition providing intermediate release (as opposed to premium release).

It is a further object of the present invention to provide controlled release additives and solventless 15 controlled release compositions particularly well suited for paper release applications.

These and other objects are accomplished herein by a controlled release additive comprising a copolymer 20 of $R_3SiO_{1.5}$ and $SiO_{4/2}$ units, where R may be the same or different monovalent hydrocarbon radical of no more than 2 carbon atoms, dispersed in an unsaturated organic reactive diluent.

25 Also contemplated herein is a solventless silicone controlled release composition comprising:

(1) a diorganopolysiloxane base polymer having up to 20% by weight alkenyl or silanol functional groups 30 and a viscosity of from about 50 to 100,000 centipoise at 25°C;

(2) a copolymer of $R_3SiO_{1.5}$ and $SiO_{4/2}$ units, where R is the same or different monovalent hydrocarbon radical 35 of no more than 2 carbon atoms, dispersed in an unsaturated

organic reactive diluent;

(3) a polymethylhydrogen siloxane fluid crosslinking agent having up to about 100% by weight SiH groups and a viscosity of about 25 to 1000 centipoise at 25°C;

(4) an effective amount of a precious metal catalyst for promoting an addition cure hydrosilation reaction between said base polymer, said copolymer and said crosslinking agent; and

(5) an amount of dialkyl carboxylic ester containing carbon-to-carbon unsaturation effective to inhibit the precious metal-catalyzed hydrosilation reaction at temperatures below the heat cure temperature of said silicone controlled release composition.

Other features of the present invention include solventless silanol-functional release compositions which have been stabilized against premature condensation of the silanol functional groups (present in amounts of about 2-5% by weight in MQ resins) in the presence of the SiH-containing crosslinker by neutralizing the silanol components in their preparation with tris(2-chloroethyl)-phosphite rather than phosphoric acid. Such compositions will have a longer shelf life, for reasons to be discussed in more detail hereinafter. Another aspect of this invention relates to silanol-functional diorganopolysiloxanes prepared by KOH-catalyzed equilibration of cyclic polysiloxane monomers and water, where the catalyst is neutralized by the introduction of tris(2-chloroethyl)phosphite so as not to produce any neutralization salts which would catalyze a condensation cure (see reaction II and discussion, infra). Also contemplated is a process for preparing silanols-functional polysiloxanes

free of latent condensation catalysts.

Other features of the present invention include
5 controlled release additives and release compositions
additionally containing vinyl-functional silicone gums.
These CRAs and compositions were found to have more stable
aged release than known controlled release formulations.

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DETAILED DESCRIPTION OF THE INVENTION

The controlled release additives of the present invention are prepared by dispersing silicone MQ resins or vinyl-functional silicone MQ resins in high-boiling unsaturated organic monomers. These CRAs may be added directly to a premium release composition to raise its release performance. For convenience, proportional amounts of a precious metal hydrosilation catalyst may be included in the CRA, so that subsequent direct addition to the release composition does not dilute the catalyst to less effective levels.

The silicone resins employed in the present invention are polysiloxanes having primarily mono-functional (M) units or tetrafunctional (Q) units. A general discussion of these resins is found in Chapters 1 and 6 of Noll, Chemistry and Technology of Silicones, 2nd Ed. 1968.

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The MQ resins are made up of M units having the formula $R_3SiO_{1/2}$ and Q units having the formula $SiO_{4/2}$, with the ratio of M to Q being roughly 0.5 to 1.0 and preferably 0.65. The R groups may be, independently, the same or different monovalent hydrocarbon radicals of no more than 2 carbon atoms. Such radicals include, for example, methyl, ethyl, vinyl or ethynyl. Methyl and vinyl are preferred.

Uncondensed MQ resins will ordinarily contain 2-5% by weight silanol, which means that contact with the precious metal catalysts which will promote the hydrosilation reaction (I), above, will also promote a silanol condensation in the presence of SiH-containing compounds, as follows:

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Silanol-containing MQ resins, therefore, will undergo a condensation cure and are suitable for use in conjunction with silanol-functional or vinyl-functional silicone

5 release compositions.

Silanol-functional polysiloxanes which will cure in the presence of SiH-containing crosslinkers and condensation catalyst to form release coatings are

10 conveniently prepared by base-catalyzed equilibration of cyclic polysiloxane monomers, such as octamethylcyclo-tetrasiloxane. The base, e.g. KOH, is commonly neutralized with phosphoric acid or silylphosphate to permit stripping the silanol products of light ends; but this mode of
15 neutralization generates acid salts (i.e., acid phosphates) which catalyze condensation of the SiOH groups with the SiH groups of the SiH-functional polysiloxane fluids used as crosslinkers in silanol release compositions. In the presence of the acid salts, therefore, a solvent-free
20 blend of silanol and SiH-containing fluids (and silanol MQ resins) quickly crosslinks to a gel and liberates hydrogen, as in reaction (II), above.

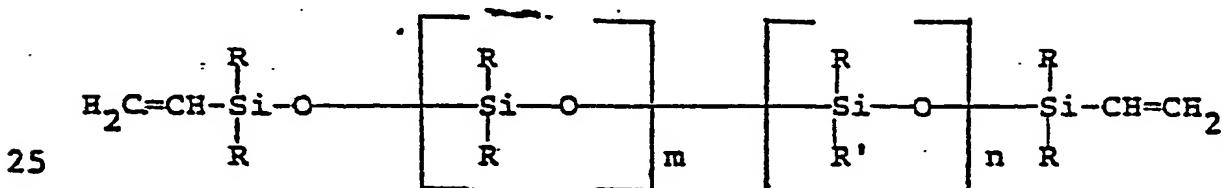
Producing silanol fluids by acid catalyzed processes
25 avoids the formation of acid salts but has proved difficult to adapt to large scale operations.

It has been discovered herein, however, that low-to-medium viscosity devolatilized silanol fluids are stable in
30 the presence of SiH-containing crosslinkers if they are neutralized with tris(2-chloroethyl)phosphite rather than by phosphoric acid. Thus in the controlled release compositions of the present invention which are based on silanol-functional diorganopolysiloxane fluids, increased storage
35 stability is achieved by neutralizing the basic hydrolysis

catalyst with tris(2-chloroethyl) phosphite.

The reactive diluents used herein to disperse the MQ resins are any high-boiling unsaturated hydrocarbon fluid in which high levels, for example, over 40% by weight, of a given MQ resin is soluble without increasing the viscosity of the dispersion beyond useful application viscosities (e.g., >5000 cps). By way of illustration, such unsaturated organic monomers will include dibutyl-
maleate, decylvinylether, dodecylvinylether, camphene, meta-bis-isopropenylbenzene and α -olefins generally. Mixtures of such compounds, and mixtures of unsaturated organic monomers with polysiloxane fluids, are also contemplated. The preferred compounds are high-boiling alpha-olefins.

In the solventless release compositions of the invention, the diorganopolysiloxane base polymer may be (as indicated previously) either silanol- or alkenyl-functional. Preferably the polymer is a vinyl chainstopped polysiloxane having the general formula:



wherein R is a monovalent hydrocarbon radical free of unsaturation, such as methyl, ethyl, propyl, butyl, and the like, but not ordinarily including phenyl for paper release applications. R' is a hydrocarbon radical having alkenyl unsaturation. Typically R' represents vinyl groups but may also represent allylic or cyclo-alkenyl unsaturated groups. m and n are positive integers such that the polymer has up to about 20% R' groups. The viscosity of such polysiloxanes will be from about 50-100,000 centipoise

at 25°C. R' is preferably vinyl and where R is vinyl, the viscosity of the polymer is preferably from about 300-550 centipoise at 25°C.

5 Methylhydrogen fluid is often used by those skilled in the silicone art as a crosslinking agent for addition-cured silicone systems. Particularly useful as a crosslinking agent for the present invention is a trimethyl chainstopped polymethylhydrogen siloxane fluid
10 having from approximately 10% to approximately 100% SiH groups and having a viscosity in the range of approximately 25 to approximately 1000 centipoise at 25°C.

15 The curing reaction which takes place between the vinyl-functional polysiloxane and the polymethylhydrogensiloxane fluid crosslinking agent is an addition cure reaction, also known as a hydrosilation. The composition of the present invention may
20 be thermally cured by means of a platinum catalyzed crosslinking reaction between pendant vinyl groups of a dialkylvinyl chainstopped polydialkyl-alkylvinylsiloxane copolymer and a trimethyl chainstopped polymethylhydrogen fluid.

25 A useful catalyst for facilitating the hydrosilation curing reaction is the Lamoreaux catalyst as described in U.S. Patent No, 3,220,972 issued November 30, 1965, and assigned to the same assignee as the present
30 invention. Other platinum-metal catalysts can also be utilized in practicing the present invention and their selection depends upon such factors as speed of the reaction required as well as expense, useful shelf-life, useful pot-life and the temperature at which the cure reaction
35 is to take place. Such platinum-metal catalysts include

those which utilize the precious metals ruthenium, rhodium, palladium, osmium, iridium and platinum, and complexes of these metals. For coating compositions as described above, the amount of catalyst ranges from

5 approximately 10 to approximately 500 ppm, depending on the factors of speed of reaction and cost. Preferably, the amount of catalyst is about 10-100 ppm of precious metal.

10 The present controlled release composition, comprising a diorganopolysiloxane base polymer, an MQ resin dispersed in a reactive diluent, a SiH-containing crosslinking fluid, and a precious metal hydrosilation catalyst, will thermally cure on a substrate and give a 15 smooth, nonadherent surface. However, it is necessary to include an inhibitor in the release composition in order to avoid premature curing and gellation of the composition. Suitable compounds to retard the hydrosilation cure reaction at ambient temperatures are well known in the 20 art, but best results have been achieved with the diallylic carboxylic esters fully disclosed in U.S. 4,256,870 (Eckberg), which is incorporated herein by reference. The preferred inhibitors are diallylmaleate, dimethylmaleate, and butyl-allylmaleate.

25 Another feature of the instant invention derives from the discovery herein that very efficient controlled release additives for solventless silicone release compositions are obtained when small amounts of vinyl-containing polysiloxane gums are included in the 30 CRA or CRA-modified release composition. The gums are vulcanizable dimethylvinyl-chainstopped linear diorganopolysiloxanes having a vinyl content of from 0.05 to 5.0 mole percent and a molecular weight ranging from about 200,000 to 800,000. The preferred gums are dimethylvinyl-chainstopped linear polydimethylmethylenesiloxane

copolymer gums having a vinyl content of approximately 0.2 mole percent and a molecular weight of around 250,000.

5 Compositions containing vinyl gums cure as rapidly as premium release compositions and have comparable release stability over time (stable aged release). This, combined with the favorable costs, raw material availability and compatibility with conventional solvent-free systems,
10 makes the vinyl gum-containing CRAs of the present invention efficient and attractive additives for controlled release applications.

In order that those skilled in the art might be
15 better able to practice the present invention, the following examples are given by way of illustration and not by way of limitation.

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EXAMPLE 1

To test the effectiveness of the control release additives of the present invention, the following 5 solventless CRAs were prepared using either uncondensed MQ resin (60% solution in toluene) or vinyl MQ resin (60% solution in xylene). In all cases, the MQ resin was mixed with an unsaturated non-volatile organic reactive diluent, the aromatic solvent was removed by vacuum at temperatures 10 below 80°C to prevent loss of the olefin component, and sufficient platinum catalyst was added to furnish approximately 100 parts per million platinum.

<u>CRA</u>	<u>Olefin Diluent</u>	<u>Resin</u>	<u>Wt. % Resin</u>	<u>Viscosit (s)</u>
15 #1	dibutylmaleate	uncondensed MQ	50	170
#2	decylvinylether	"	50	27
#3	dibutylmaleate	"	60	765
#4	dodecylvinylether	"	60	110
20 C(i)	vinyl-stopped dimethyl fluid*	"	50	420,000
C(ii)	vinyl-stopped dimethyl fluid*	"	37½	1,850
#5.	64% camphene, 36% vinyl stopped dimethyl fluid*	"	60	280
25 #6	64% C ₍₁₆₋₁₈₎ alpha-olefin, 36% vinyl-stopped dimethyl fluid*	"	60	750
#7	64% C ₍₁₆₋₁₈₎ alpha-olefin, 36% vinyl-stopped dimethyl fluid*	"	60	800
30 #8	meta-bis-isopropane-benzene	"	—	220
#9	alpha-olefin + vinyl gum**	"	—	450

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- * 200 centipoise dimethyl vinyl-chainstopped linear polydimethylsiloxane fluid
- ** 105 parts of a C₁₆-C₁₈ alpha-olefin mixture (Ethyl Corporation) plus 15 parts of a dimethylvinyl-chainstopped linear polydimethylmethoxane copolymer gum (0.2 mole % vinyl, 250,000 average molecular weight; General Electric Co.)

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In order to determine the effect of the CRAs on cure, the following coating baths were made up:

10	Base Polymer*	CRA, (Parts by Weight)	Cross-Linker** (Parts by Weight)
#1	7.5	#1, 2.5 1.25 Resin 1.25 Solvent	0.5
#2	7.5	#2, 2.5	0.5
#3	7.5	#3, 2.5	0.5
15 #4	7.5	#4, 2.5	0.5
#5	8	#9, 2	0.5
#6	8	#8, 2	0.5
C(iii)	10	--	0.5
C(iv)	10	--	0.4

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- * base polymer equals vinyl-stopped dimethyl polysiloxane fluid plus a vinyl gum cure accelerator, prepared according to commonly assigned copending U.S. Application Serial No. 267,091, filed May 22, 1981 (incorporated herein by reference), platinum catalyst (~150 ppm Pt) and dimethyl maleate
- 25 ** cross-linker equals: low viscosity methyl chainstopped polylinear polymethyl hydrogen siloxane fluid

30 These coating baths were applied to 40 pound supercalendered kraft paper substrates, placed in a 120°C forced air oven until the coating compositions cured to a smear- and migration-free adhesive surface. The minimum cure time was determined:

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	<u>Bath</u>	<u>Cure Time (sec)</u>
5	#1	10
	#2	10
	#3	20
	#4	30
	#5	30
	#6	35
10	C(iii)	10
	C(iv)	30

It can be seen that the MQ resin content slows cure but does not prevent cure in this system.

15 In order to assess the efficiency of the CRA compositions in terms of release, it was necessary to coat out of solvent. The following solutions were prepared:

		<u>Hexane</u> <u>Bath (parts by weight)</u>	<u>Base Polymer</u> <u>(parts by weight)</u>	<u>CRA</u> <u>(parts by weight)</u>	<u>Cross-Linker</u> <u>(parts by weight)</u>
20	a	80.0	20.0	(no CRA)	1
	b	80.0	15.0	conventional CRA*	1
	c	80.0	15.0	#5, 5	1
	d	80.0	15.0	#6, 5	1
	e	80.0	15.0	#7, 5	1
	f	80.0	15.0	#1, 5	1
25	g	80.0	15.0	#2, 5	1
	h	80.0	15.0	#3, 5	1
	i	80.0	15.0	#4, 5	1
	j	80.0	16.0	#9, 4	1
	k	80.0	16.0	#8, 4	1
	l	80.0	16.0	conventional CRA, 4	1

* 3 parts vinyl MQ resin dissolved in low viscosity vinyl-functional dimethylpolysiloxane

35** a vinyl-stopped dimethyl polysiloxane with vinyl gum cure accelerators, platinum catalyst and dimethylmaleate inhibitor (grade SS-4310; General Electric Co.)

Each bath was coated onto 40 pound kraft paper with a No. 3 wire-wound rod, then placed in a 120° forced air oven for 30 seconds to insure complete cure.

5 The cured silicone-coated paper was laminated with 5 mil of Coated Products' #4950 SBR pressure sensitive adhesive which was dried for 10 minutes at ambient temperatures, then for 6 minutes at 60°C. A second sheet of kraft paper was placed atop the adhesive layer, and 10 2" x 9" tapes of the resulting laminates were prepared. A Scott tester was used to record the force (in grams) required to separate the silicone lamina from the adhesive lamina when the laminae were pulled apart at a 180° angle at 400 ft/min. Release was also recorded for 15 tapes aged 2 weeks at room temperature.

Quantitative release observed is tabulated below:

<u>Release, grams</u>			<u>Aged Differential Release</u> <u>(grams)*</u>
	<u>Initial</u>	<u>Aged</u>	
20	A	20-40	20-30
	B	50-70	65-95
	C	80-110	100-150
	D	90-120	110-160
25	E	80-100	80-120
	F	70-100	160-210
	G	100-130	190-250
	H	65-85	150-180
30	I	65-95	175-225
	J	60-80	80-85
	K	55-75	70-95
	L	40-60	60-70

* Aged differential release = (average release - average release of unaltered release composition (Bath A)).

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EXAMPLE 2

In order to demonstrate the neutralization of the KOH-catalyzed preparation of silanol-functional materials, 5 the following samples were prepared:

Sample A

3500 parts by weight of dimethyl cyclic tetramer 10 plus 0.20 parts by weight finely-ground KOH were placed in a 5 liter flask and heated to 150-155°C for 90 minutes. The liquid then began to rapidly build in viscosity and 10 parts by weight of water were added. Equilibration was continued for 3 more hours at 150-155°C, resulting in a 1600 cps 15 viscosity fluid which measured 34.7 ppm KOH by titre. The hot equilibrate was treated with 0.18 parts by weight of tris(2-chloroethyl)phosphite and the mixture held at 150° for 30 minutes. Prior to stripping, the tris(2-chloroethyl)-phosphite treated polymer titred slightly basic (<3 ppm KOH). 20 Stripping the silanol fluid under full vacuum (about 10 mm Hg pressure) at 160-180°C for two hours afforded 2700 parts by weight of a 2850 cps viscosity polymer. Processing was completed by adding 89 parts by weight of a 30 cps viscosity methylhydrogen crosslinker, stirring until uniform, and 25 filtering. The product (Sample A) was a water-white 100% solids silicone blend, 2325 cps viscosity, containing 97% silanol-stopped dimethylsilicone fluid and 3% polymethylhydrogen crosslinker.

Sample B

3422 parts by weight of cyclic tetramer, 0.3 parts by weight KOH, and 146 parts by weight of a very-low-viscosity silanol-stopped linear dimethyl fluid containing about 8 weight % water as chainstopper were placed into a flask. This mixture formed a viscous polymer after 40 minutes at 153°C. Neutralization was accomplished by addition of 0.54 parts by weight tris(2-chloroethyl)phosphite and 10 stirring at 150°C for two hours. Light ends were removed by stripping to yield 3040 parts by weight of silanol fluid to which 101 parts by weight methylhydrogen crosslinker were added. The filtered product (Sample B) was a clear viscous mixture, 5250 cps in viscosity.

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Sample C

A control was prepared by mixing 3:3 parts of methylhydrogen fluid with 100 parts of a silanol-stopped linear dimethyl fluid prepared by KOH equilibration and phosphoric acid neutralization (similar to examples 1 and 2 except that a molar equivalent amount of H_3PO_4 was substituted for tris(2-chloroethyl)phosphite.

10 The performance of the 3 samples described above was compared to the performance of commercial silanol composition (General Electric Co.) prepared by acid-catalyzed equilibration of cyclic tetramer and water (Sample D below). Shelf stability was measured by monitoring the viscosity of the compositions 15 as a function of time as they were stored at room temperature ($25^\circ C$). Results obtained are presented below:

<u>Composition</u>	<u>Initial Viscosity, cps.</u>	<u>1 Month cps.</u>	<u>2 Month cps.</u>	<u>4 Month cps.</u>	<u>6 Month cps.</u>
A	2325	2290	2280	2360	2332
20 B	5250	4900	5300	5300	5300
C	3100	>100,000	gel	—	—
D	3800	3880	3950	4300	4700

These 4 samples were tested for release 25 performance in the same manner as Example 1, except that the compositions were applied to the kraft paper out of a Lexane solvent with a No. 12 wire-wound rod and cured in a $150^\circ C$ oven for 30 seconds. The following results were observed:

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<u>Composition</u>	<u>Measured Release (parts by weight)</u>
A	150-170
B	145-170
C	150-175
5 D	130-165

It can be seen that the silanol-functional compositions neutralized according to the present invention (Samples A and B) have a longer shelf-life than conventionally-
10 neutralized silanol polymethylhydrogensiloxane compositions.

Obviously, many variations will suggest themselves to those skilled in this art in light of the above, detailed description. All such modifications
15 are within the intended scope of the appended claims.

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Claims:

1. A controlled release additive comprising a copolymer of R_3SiO_x units and $SiO_{4/2}$ units, where R 5 represents the same or different monovalent hydrocarbon radical of no more than 2 carbon atoms, dispersed in an unsaturated non-volatile organic reactive diluent.

2. The controlled release additive of Claim 1, 10 wherein said copolymer is an uncondensed silicone MQ resin and said reactive diluent is selected from the group consisting of dibutyl maleate, decylvinylether, dodecyl-vinylether, camphene, $C_{(16-18)}$ alpha-olefin and meta-bis-isopropenylbenzene:

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3. The controlled release additive of Claim 1, wherein said copolymer is a vinyl silicone MQ resin and said reactive diluent is a $C_{(16-18)}$ alpha-olefin mixture.

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4. The controlled release additive of Claim 1 which also contains a small amount of a vinyl-containing polysiloxane gum.

5. A solventless silicone controlled release 25 composition comprising:

(1) a diorganopolysiloxane base polymer having up to 20% by weight of SiH groups or silanol-functional groups and a viscosity of 30 from about 50 to about 100,000 centipoise at 25°C;

5 (2) a copolymer of R_3SiO_3 and $SiO_4/2$ units, where R is the same or different monovalent hydrocarbon radical of no more than 2 carbon atoms dispersed in an unsaturated organic reactive diluent;

10 (3) a polymethylhydrogen siloxane fluid crosslinking agent having up to about 100 parts by weight SiH groups and a viscosity of about 10 25 to 1,000 centipoise at 25°C;

15 (4) an effective amount of a precious metal catalyst for promoting an addition cured hydrosilation reaction between said copolymer, said additive and said crosslinking agent; and

20 (5) an amount of dialkyl carboxylic ester containing carbon-to-carbon unsaturation effective to exhibit said hydrosilation reaction at temperatures below the heat cure temperature of said silicone controlled release composition.

25 6. The composition of Claim 5, wherein said base polymer is a vinyl-chainstopped polydimethylmethylviny siloxane copolymer.

30 7. The composition of Claim 5, wherein said copolymer component (2) is an uncondensed silicone MQ resin and said reactive diluent is selected from the group consisting of dibutyl maleate, decylvinylether, dodecylvinyl-ether, camphene, $C_{(16-18)}$ alpha-olefin and meta-bis-isopropenyl-benzene.

8. The composition of Claim 5, wherein said copolymer component (2) is a vinyl silicone MQ resin dispersed in C₍₁₆₋₁₈₎ alpha-olefin.

5 9. The composition of Claim 5 which also contains a small amount of a vinyl-containing polysiloxane gum.

10. The composition of Claim 5, wherein the base polymer is silanol-functional and was prepared by a KOH-
10 catalyzed equilibration of octamethylcyclotetrasiloxane and water, neutralized by the addition of a small amount of tris(2-chloroethyl)phosphite.

11. A silanol-functional diorganopolysiloxane
15 composition free of latent condensation catalyst having up to about 20% by weight SiOH groups and a viscosity of from about 50 to about 100,000 centipoise at 25°C prepared by a base-catalyzed equilibration of cyclic polysiloxane monomers and water, said base being neutralized by the addition of
20 tris(2-chloroethyl)phosphite.

12. A silanol-functional diorganopolysiloxane composition as defined in Claim 11, wherein said base is KOH and said cyclic polysiloxane monomers are primarily
25 octamethylcyclotetrasiloxane.

13. A process for preparing a silanol-functional diorganopolysiloxane free of latent condensation catalyst and having up to about 20% by weight SiOH functional groups
30 and a viscosity of from about 50 to about 100,000 centipoise at 25°C comprising (a) equilibrating cyclic polysiloxane monomers and water in the presence of a base and (b) neutralizing the base with tris(2-chloroethyl)phosphite.

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14. The process of Claim 13, wherein said cyclic polysiloxane monomers are primarily octamethylcyclotetrasiloxane and said base is KOH.

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EUROPEAN PATENT APPLICATION

⑬ Application number: 83108448.8

⑮ Int. Cl.³: C 08 L 83/04

⑭ Date of filing: 27.08.83

C 09 J 7/02
//(C08L83/04, 83/04)

⑯ Priority: 10.09.82 US 416576

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⑯ Date of publication of application:
16.05.84 Bulletin 84/20

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⑯ Date of deferred publication of search report: 18.07.84

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⑯ Designated Contracting States:
AT BE DE FR GB IT NL

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⑯ Solventless silicone controlled release compositions.

⑯ Controlled release additives are provided which are useful to raise the release of low-release solventless silicone release compositions. Solventless silicone release compositions are also provided. The aged release of controlled release compositions may also be enhanced by addition of a small amount of a vinyl polysiloxane gum.

EP 0 108 208 A3



DOCUMENTS CONSIDERED TO BE RELEVANT		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages		
Y	<u>GB - A - 2 073 765</u> (GENERAL ELECTRIC) * Claims 1,2,3,8 * --	1-8	C 08 L 83/04// (C 08 L 83/04 83/04) C 09 J 57/02 C 08 G 77/34 C 08 G 77/08
Y	<u>FR - A - 2 450 642</u> (DOW CORNING) * Claim 1; page 14, lines 30-37; page 15, line 1 * --		
Y	<u>GB - A - 1 055 777</u> (DOW CORNING) * Claims 1,2; page 3, lines 66-85 * --	1	
Y	<u>GB - A - 2 022 115</u> (DOW CORNING) * Claim 1 * --	1	TECHNICAL FIELDS SEARCHED (Int. Cl. ³)
Y	<u>GB - A - 2 051 101</u> (DOW CORNING) * Claims 1,2 * --	1	C 08 L C 09 J C 08 G
A	<u>US - A - 4 347 346</u> (R.P. ECKBERG) * Claims 1,6,7,10 * --	1	
X	<u>GB - A - 2 052 539</u> (GENERAL ELECTRIC) ./.		
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 05-04-1984	Examiner DEPYPER
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid.
namely claims:
- No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.



LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

- 1) Claims 1-9: a controlled release additive and a solventless silicone release composition containing these additive.
- 2) Claims 10-14: a silanol-functional diorganopolysiloxane and a process for preparing this polysiloxane.



All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.



Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid.

namely claims:



None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.

namely claims:



European Patent
Office

EUROPEAN SEARCH REPORT

0108208

Application number

EP 83 10 8448 -2-

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	* Claims 1,3,10,14; page 3, lines 59-60; page 5, lines 35-40 * -- X GB - A - 2 065 153 (GENERAL ELECTRIC) * Claims 1,8 * -----	10-14	
		10-14	TECHNICAL FIELDS SEARCHED (Int. Cl.)